

Supporting information for

# ***N*-Phthaloyltranexamic Acid Ammonium Salt Derivatives as Photocaged Superbase for Redox Free Radical Photopolymerization**

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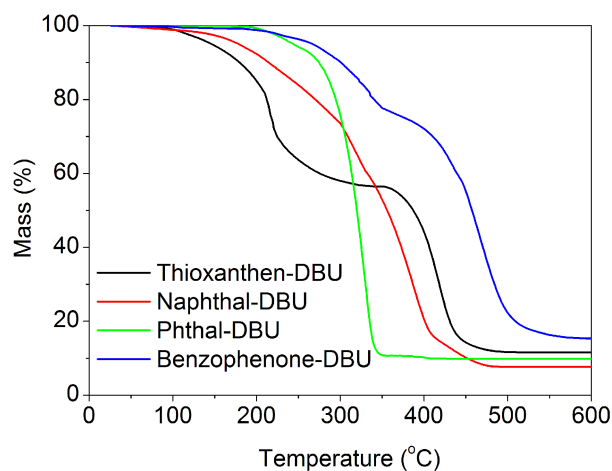
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## 1 Thermogravimetric profiles of photocaged bases



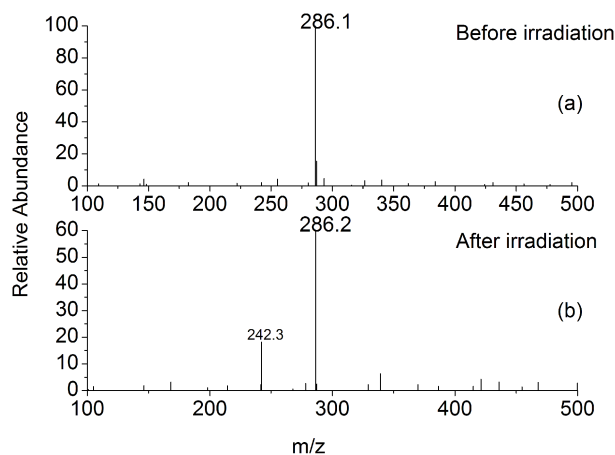
**Figure s1.** Thermogravimetric profiles of photocaged bases with heating rate at 20 °C/min under N<sub>2</sub>.

**Table S1.** Thermal stability of photocaged bases

Photocaged bases	TG (°C) <sup>a</sup>
Phthal-DBU	244.2
Naphthal-DBU	178.4
Benzophenone-DBU	267.1
Thioxanthen-DBU	146.4

<sup>a</sup> Determined by thermogravimetric analysis as the point of 5% weight loss.

## 2 The protonated *N*-phthalimido-amino acid detected by ESI-MS

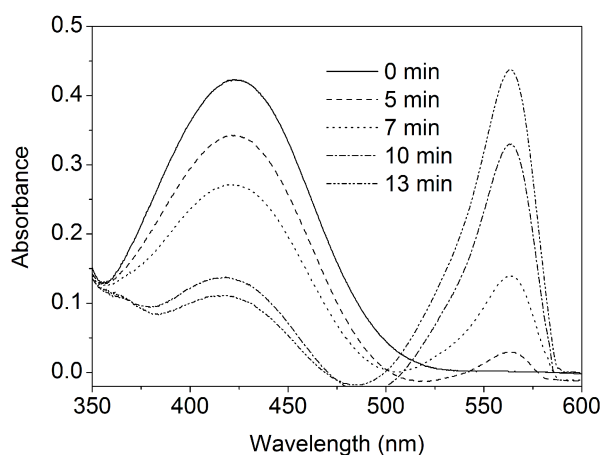


**Figure s2.** Positive ion ESI-MS spectra of Phthal-DBU in DMSO (0.01 mM) (a) before and (b) after irradiation.

### 3 Photogenerated basic compounds detected by phenol red

Photocaged base (Phthal-DBU) solution in acetonitrile ( $1 \times 10^{-4}$  M, 0.75 mL) was put into a tube with a quartz cell, after the solution in the quartz cell was irradiated with time by a medium-pressure mercury lamp, and then an aqueous solution of phenol red (0.75 mL,  $1 \times 10^{-5}$  M) was added, UV spectra of the aqueous solution were measured. The light intensity was measured as  $20 \text{ mW/cm}^2$  at 365 nm.

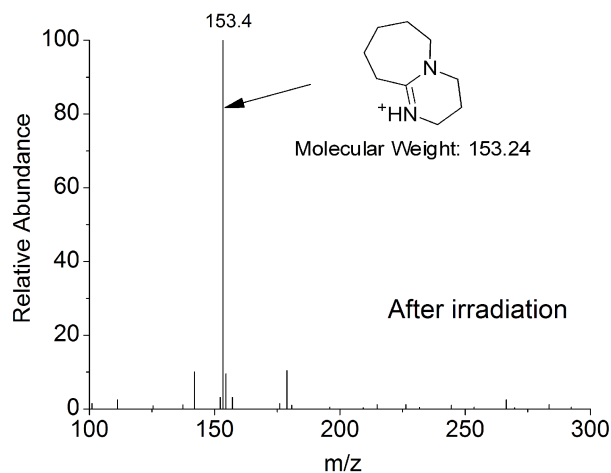
It is well known that the aqueous solution of phenol red shows an absorption band at 430 nm at  $\text{pH} < 7.0$  and that the absorption band shifts to 560 nm due to a quinoid structure at  $\text{pH} > 7.0$ . As shown in **Figure s3**, no absorption band changes at 430 nm in the aqueous solution were observed with the addition of nonirradiated Phthal-DBU solution, upon addition of irradiated solution induced a new absorption band at 560 nm, assigned to the deprotonated phenol red after reaction with the released amine, and the intensity increased with the irradiation time. This fact shows that basic compounds were produced in the photolysis.



**Figure s3.** UV spectral changes in an aqueous solution of phenol red upon addition of a solution of Phthal-DBU in AN being irradiated over time.

### 4 Protonated DBU detected by ESI-MS

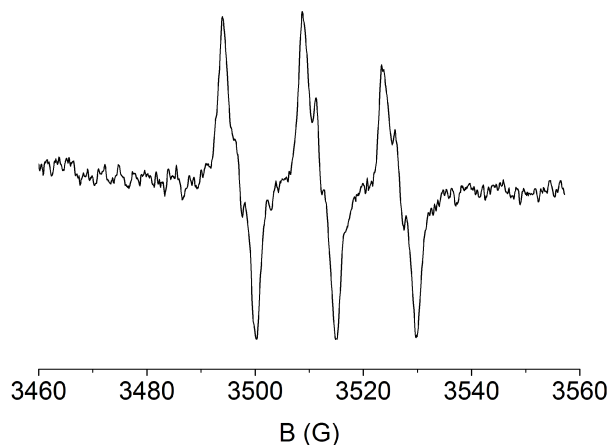
Phthal-DBU solution in DMSO (0.02 mM) was irradiated 30 min, and then isometric water was added. Because Phthal-DBU is insoluble in water, and then the obtained mixture was filtrated to remove the nonphotolytic Phthal-DBU. ESI-MS spectra of the filtrated solution were measured, as shown in **Figure s4**.



**Figure s4.** Positive ion ESI-MS spectra of Phthal-DBU in DMSO (0.01 mM) after irradiation.

### 5 ESR-spin trapping spectrum of DBU&BPO

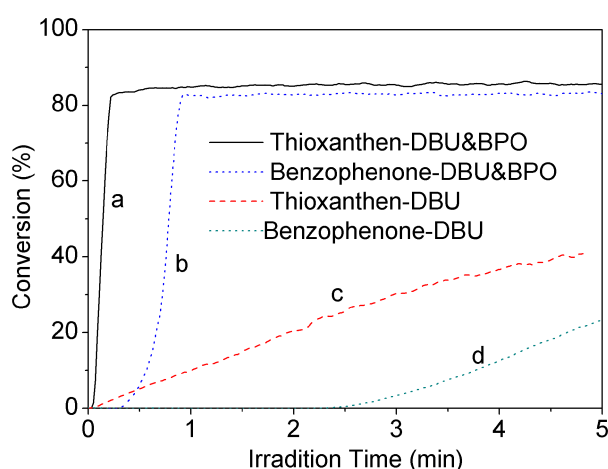
The ESR spectra were obtained on an Electron Paramagnetic Resonance Spectrometer (Bruker Biospin). To BPO in DMSO was slowly added DBU in DMSO, the radicals were produced, and then trapped by phenyl-N-tert-butyl nitron (PBN, TCI Company). As shown in **Figure s5**, upon blending of DBU with BPO, the formation of two radicals is clearly observed in ESR spin trapping experiments.



**Figure s5.** ESR-spin trapping spectrum of DBU&BPO in DMSO, [DBU] = [BPO] = 0.01 M, [PBN] = 0.02 M.

## 6 The comparison between photocaged redox combination and photocaged base

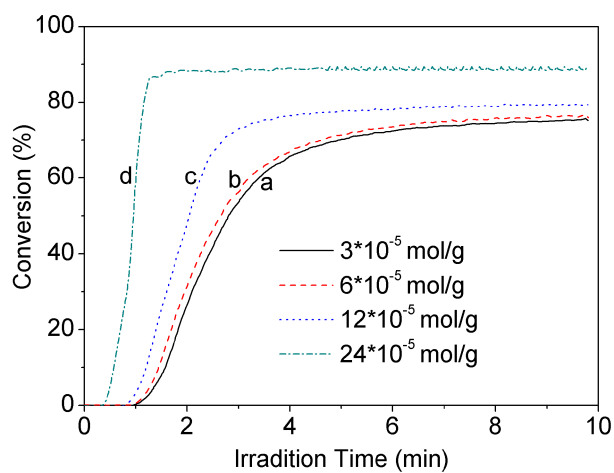
The similar phenomenon also can be observed in other photocaged redox combinations such as Thioxanthen-DBU&BPO and Benzophenone-DBU&BPO. As depicted in Figure s6, the catalytic behavior of photocaged redox combinations (Thioxanthen-DBU&BPO, Benzophenone-DBU&BPO), and its parent compounds (Thioxanthen-DBU, Benzophenone-DBU), were compared by real-time Fourier transform infrared (FTIR) spectroscopy at room temperature. The photopolymerization of TMPTA in the presence of Thioxanthen-DBU or Benzophenone-DBU was also slow, 40% and 23% final conversion were obtained in 5 min, respectively. On the other hand, in the presence of the photocaged redox initiation, excellent polymerization profiles were obtained.



**Figure s6.** Conversion vs time for the photopolymerization of TMPTA in the presence of: (a) Thioxanthen-DBU&BPO, (b) Benzophenone-DBU&BPO, (c) Thioxanthen-DBU, and (d) Benzophenone-DBU, [Photocaged base]:[BPO] = 1:1, [Phthal-DBU] =  $3 \times 10^{-5}$  mol, TMPTA = 1 g, DMSO = 0.5 mL.

## 7 Effect of BPO concentration

The concentration of the peroxide initiator is also one of important factors in redox photopolymerization. When the peroxide concentration is too low, it is not possible to start a faster initiation rate. On the contrary, if the concentration of the initiator is very high, the pot life may be short, making the system less useful. Having established that BPO is the most potent of the four peroxides examined, the effect of [BPO] is evaluated next. **Figure s7** shows the experimentally determined kinetic profiles in the presence of varied BPO concentration. As expected, increasing the catalyst concentration results in an increase in the photosensitivity. Namely, an increase in the BPO concentration from  $3 \times 10^{-5}$  mol to  $24 \times 10^{-5}$  mol caused a decrease of both  $T_{start}$  from 0.93 min to 0.36 min, and an increase final conversion from 75% to 89%, respectively.



**Figure s7.** Effect of BPO concentrations on the conversion vs time for the Phthal-DBU&BPO-initiated photopolymerization. (a)  $3 \times 10^{-5}$  mol/g, (b)  $6 \times 10^{-5}$  mol/g, (c)  $12 \times 10^{-5}$  mol/g, (d)  $24 \times 10^{-5}$  mol/g, [BPO] =  $3 \times 10^{-5}$  mol, TMPTA = 1 g, DMSO = 0.5 mL.